

NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN

SERIES OF GEOLOGY AND TECHNICAL SCIENCES

ISSN 2224-5278

Volume 1, Number 439 (2020), 38 – 47

<https://doi.org/10.32014/2020.2518-170X.5>

UDC 662.73

ISRSTI 61.53.91

B. T. Yermagambet, N. U. Nurgaliyev, N. A. Maslov, L. D. Abylgazina, A. A. Syzdykova

Institute of Coal Chemistry and Technology LLP, Nur-Sultan, Kazakhstan.

E-mail: coaltech@bk.ru, bake.yer@mail.ru, nurgaliyev_nao@mail.ru, nike.6484@mail.ru,

lelya_1501@mail.ru, botasyzdykova2212@gmail.com

**EFFECT OF ELECTROPHYSICAL IMPACT
ON THE PHYSICAL AND CHEMICAL CHARACTERISTICS
OF COAL ASH FROM THE MAIKUBEN DEPOSIT**

Abstract. The paper studies the effect of electrophysical treatment of ash from coal of Maikuben deposit on its physical and chemical characteristics. The processing of coal ash was carried out on an electromagnetic apparatus (for fine grinding of ash particles) and on a high-voltage electric discharge installation (to change the properties of ash). The physical and chemical characteristics of coal ash were studied by multi-element instrumental neutron activation analysis (elemental analysis on the content of microelements), energy dispersive X-ray spectroscopy on a scanning raster electron microscope with an attachment for energy dispersive analysis (for studying the structure and size of ash and analyzing the content of macroelements), laser diffraction (for analyzing the volume distribution of ash particles size), Brunauer-Emmett-Teller (BET) (for determining the specific surface area and pore volume). It was established that after the electromagnetic treatment of coal ash, the surface of the samples acquires a more developed and porous structure and the particle sizes significantly decrease. This is especially observed for the average volumetric distribution of $D_v(50)$ (50% of particles of their total number), where the interval of change of particles is 129-7 micrometers. As a result of the electric discharge treatment of coal ash, additional mineral complex compounds are formed with the content of some rare metals Ga, Ge, Li. It was revealed that the electric discharge treatment of ash, like the electromagnetic treatment, leads to a decrease in the size of the particles of the original ash, but not so significantly (up to 1.3 times).

Key words: coal, ash, electromagnetic treatment, electric discharge treatment, chemical composition, physical and chemical characteristics.

Introduction. Ash and slag waste (ASW) of coal-fired thermal power plants can be considered as technogenic deposits of mineral substances suitable for cost-effective industrial use.

ASW are products of high-temperature (1200-1700°C) processing of the mineral part of the fuel [1]. The main ash-forming macronutrients in ASW (Si, Al, Fe, O, Ca, Ti, Mg, S, K, Na) make up 98-99%. Particularly all other elements (trace elements) are contained in the ash in a concentration of 0.1% or less. During the combustion of coal, part of the trace elements (Sr, Ba, Sc, Y, La, Ti, Zr, etc.) is concentrated in the slag. Other elements (Ga, In, Tl, Ge, Sn, Pb, etc.) at temperatures above 1000°C volatilize from the zone of high temperatures and settle in electrostatic precipitators and cyclones (at 110–120 °C) [1]. Moreover, the chemical properties of the ash and slag waste system vary greatly depending on the type of coal, combustion temperature, combustion technology, air / fuel ratio, and coal particle size [2].

All elements of ASW can be part of both the mineral part of the coal (i.e. form minerals) and in the form of compounds with the organic matter of the coal, forming the so-called organic-mineral components, which are the least studied forms. These include: salts of humic acids (K, Na, Ca, Mg, etc.), complex humates, characterized by a cyclic system of bonds, as well as organic compounds (i.e., C-E bond, where E is S, Si etc.) [3].

A significant accumulation of ash and slag waste due to coal combustion (in CHP, boiler houses) in ash dumps causes special attention to the study of the physical and chemical characteristics of coal ash.

For example, in [3-8], coal ash was studied using elemental, electron microscopic, X-ray phase analysis, and particle size analysis. These studies have shown that the ash contains mainly silicon dioxide, aluminum oxide and iron oxide and is a fine amorphous material consisting of particles with a size of 5-100 microns. Fly ash consists of glassy, hollow spherical particles, which are cenospheres (thin-walled hollow spheres). The mineralogical composition of ash is represented mainly by inorganic elements in the form of quartz, kaolinite group minerals, mullite, magnetite, siderite, hematite. The modulus of ash basicity is basically $MO < 1$, therefore, this ash is classified as acidic, which results in the absence of binding properties of these materials. Studies of the sorption properties of coal ash showed that the specific surface area of ash (measured by the BET method) can vary from 1.1 to 15.6 m²/g, depending on the phase content and porosity [9-13]; while the total pore volume can vary from 0.004 to 0.022 cm³/g [10,12].

The specific properties of ash and slag waste are used in the production of building materials (as additives in concrete, cement, bricks, etc.) [1,14,15], in the preparation of aluminosilicate and magnetic microspheres [1], silica [16] and alumina [17,18], in the extraction of rare metals [19-24].

The purpose of this work is to study the effect of electrophysical effects on the physicochemical characteristics of the ash of Maikuben coal. Experiments were performed in LLP "Institute of Coal Chemistry and Technology" (Astana).

As objects of research, ash was used in its original form, ash after processing on an electromagnetic device (hereinafter EM treatment) and ash after electric discharge treatment (hereinafter ED treatment) (except for samples for analyzing the size of coal ash particles, where the processing was carried out separately from friend to determine the impact of each influence). EM treatment of coal ash was carried out for its fine grinding, the ED treatment of ash to weaken and/or break chemical bonds in an aqueous solution of ash.

Research methodology. The preparation of ash samples was carried out in 3 stages. At the 1st stage, the ash was pre-crushed and an average sample (by chemical and particle size distribution) was prepared from the combined sample *кварт* by the quartering method. At the 2nd and 3rd stages, the EM processing and then the ED treatment were carried out, respectively.

EM processing of ash samples was carried out on an electromagnetic apparatus EMA-1 (figure 1), which consists of an inductor, a working chamber and a tripod. Electric parameters of EMA-1: rated current - 8 Amps; nominal electromagnetic field strength in the center of the inductor (at 220 V) – 40-45 kA/m; active power – 0.15-0.2 kW; the power and capacity of capacitors to compensate for $\cos\varphi$ is 400 microfarads.

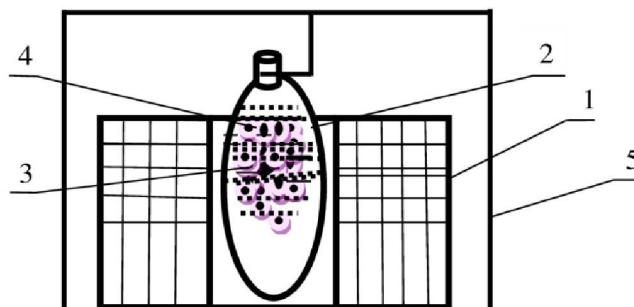


Figure 1 – Grinding of ash in EMA-1 in the periodic mode: 1 – inductor; 2 – working chamber; 3 – magnetic granules; 4 – crushed material; 5 – tripod

The treatment was carried out as follows:

- coal ash (100 grams) was mixed with magnetic granules (2-3 mm in diameter) (the ratio of the mass of the ground material to the mass of magnetic granules 1:10; magnetic granules occupied 70-80% by volume of the working chamber);

- a glass beaker was placed in the working chamber (about 1 l), in which an elastic material (rubber-fabric was preliminarily inserted inside) to prevent sticking of the crushed ash to the walls and the formation of cracks on the walls of the glass from the impact of magnetic granules);

- the resulting mixture of ash with magnetic granules was unloaded in the working chamber and closed (to prevent the ash from entering the atmosphere);
- the working chamber was installed inside the inductor (in the middle);
- electromagnetic processing in EMA-1 was performed 3 times for 8 minutes;

At the same time, during processing in the chamber thorough mixing and grinding of ash occurred due to the strong rotating and colliding actions of the magnetic granules, which is caused by the induction of the vortex electric field due to the action of the alternating electromagnetic field from the inductor.

Visually, it was found that the size of the ash particles after electromagnetic treatment decreased significantly compared with the particles of the original ash.

ED treatment of coal ash by high-voltage pulsed discharge was carried out in a laboratory electric discharge installation (figure 2), consisting of the following components: power regulator, capacitor bank, step-up transformer (from 220 V to 30 kV), reactor (200 ml capacity for coal water solution ash with 2 electrodes).

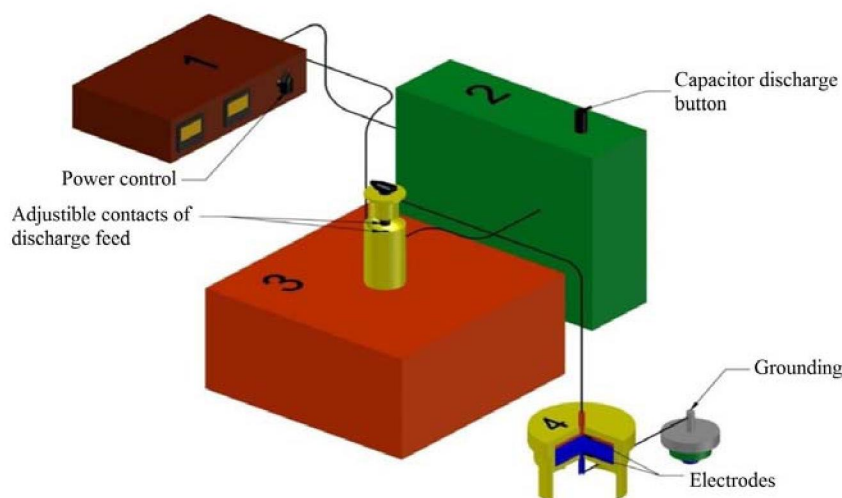


Figure 2 – Schematic diagram of the electric discharge installation

Experiments were performed as follows. The necessary technical parameters were pre-installed and adjusted (voltage 30 kV, the number of discharge into the reactor 5 times in 1 second, the distance between the upper electrode and the surface of the solution was 3-5 mm). The prepared ash weighing 40 g and 80 ml of water were thoroughly mixed and the resulting solution was poured into the reactor. The installation was turned on through a special remote control and arc-processed for 3 minutes. Next, the resulting solution was dried to a dry state (for the subsequent measurement of the electrophysical characteristics of coal ash).

Elemental analysis of the content of microelements in the Maikubensky coal was performed using multi-element instrumental neutron activation analysis on a multichannel amplitude pulse analyzer (KANBERRA) with a detector of pure germanium mark GX-3018 with a resolution of 1.8 keV using the Co60 line of 1333 keV and recording efficiency 30 %

The study of the elemental composition, structure and dimension of coal ash was carried out using energy dispersive X-ray spectroscopy on a scanning electron scanning microscope SEM (Quanta 3D 200i) with an attachment for energy dispersive analysis (EDAX). The samples were attached to a copper holder with conductive adhesive paper. Previously, a thin conducting layer of carbon was deposited on the surface of the samples in a special vacuum unit for better passage of charges. The energy of the exciting electron beam in the analysis was 15 keV, the working distance was 15 mm.

X-ray diffraction was used to identify the crystalline phases that make up the ash. X-ray phase analysis was performed on a Rigaku MiniFlex 600 diffractometer. The sampling mode: Fe, K β -radiation, voltage on the X-ray tube is $U = 40$ kV with a current $J = 15$ mA.

The adsorption characteristics of the ash (specific surface area, specific volume by limiting filling) were studied using the Brunauer – Emmett – Teller method (BET). The measurements were performed on a Sorbtometer M analyzer (CATACON company). Nitrogen was used as adsorbate gas, helium was used

as carrier gas. Before starting the measurement of the sample, a thermal training was performed, i.e. its degassing, which consists in heating the sample in a stationary gas flow at a given temperature in order to remove absorbed gases and vapors from the surface of the material under study.

To establish the degree of influence of electrophysical effects on the particle size of coal ash, an analysis of the volume distribution of particle sizes was carried out for various values of bulk density. At the same time, the processing of coal ash by an electric discharge and an electromagnetic method was carried out separately from each other, in order to exclude their mutual influence, and thus to conduct a comparative analysis of the effectiveness of each type of influence on the particle size. Analysis of ash particle sizes was performed by laser diffraction using a *Malvern Mastersizer 3000* instrument, designed to obtain information about the volume distribution of particle sizes in the range from 0.01 to 10 000 μm . Distilled water was used as a dispersant for all ash samples in the Hydro-MV mode.

Results and its discussion. The results of the elemental analysis show the presence of 31 micro-elements in ash samples of Maikuben coal (table 1).

According to the technical classification [23], the following groups of rare metals are present in coal samples: light – Cs, Li, Rb, Sr, Ba; refractory – Ta, Hf; rare earth metals – Sc, La, Nd, Eu, Tb, Yb, Lu, Sm, Ce; scattered – Ga, Ge, Cd; radioactive – U, Th.

As can be seen from the listed metals, predominantly rare earth metals are present in the coal.

Table 1 – Results of multi-element instrumental neutron activation analysis of the studied Maikuben coal

Sample number	Element	Content, g/t
1	Samarium (Sm)	10.5
2	Uran (U)	2.0
3	Ytterbium (Yb)	5.82
4	Bromine (Br)	<1
5	Lantan (La)	51.0
6	Cerium (Ce)	90.5
7	Terbiy (Tb)	2.47
8	Chromium (Cr)	82.5
9	Barium (Ba)	2341
10	Strontium (Sr)	1622
11	Silver (Ag)	<0.5
12	Rubidium (Rb)	45.4
13	Cobalt (Co)	33.6
14	Neodymium (Nd)	61.5
15	Gallium (Ga)	21.85
16	Zinc (Zn)	136.6
17	Thorium (Th)	8.5
18	Hafnium (Hf)	8.20
19	Tantalum (Ta)	0.1
20	Germanium (Ge)	16.48
21	Calcium (Ca)	3.54
22	Lutetium (Lu)	0.81
23	Gold (Au)	0.0089
24	Arsenic (As)	14.3
25	Sodium (Na)	0.08
26	Scandium (Sc)	31.1
27	Iron (Fe)	7.24
28	Europium (Eu)	3.30
29	Lithium (Li)	12.92
30	Cesium (Cs)	3.22
31	Cadmium (Cd)	5.72
Note: content of Fe, Ca, Na in %.		

Analysis of the obtained results shows the presence in the greatest amount (from 0.08 to 3.54%) of metals such as calcium, barium, strontium, sodium (in decreasing order of concentration), attracting a certain interest for industry. Their concentrations (in wt.%) Are: Sr (0.1622), Ba (0.2341), Na (0.08), Ca (3.54). The remaining elements are present in very small quantities (from 0.01% or less), especially silver, tantalum, gold, bromine, lutetium (to 0.0001%).

The results of elemental energy dispersive analysis (EDAX) on the content of macronutrients in the ashes of (initial) coals are shown in table 2.

Table 2 – The chemical composition of the mineral part of Maikuben coal

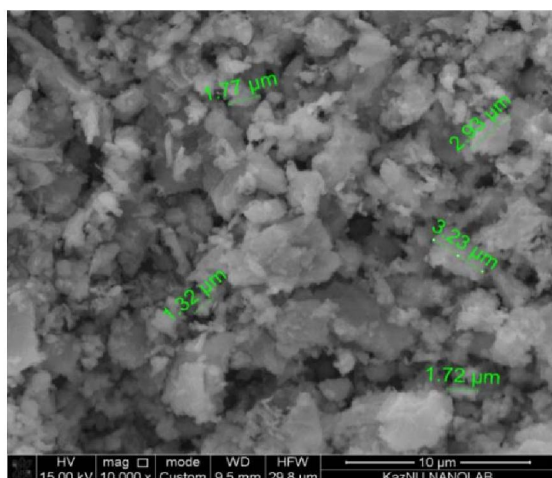
Indicators	Content, wt. %
SiO ₂ , %	50.16
Al ₂ O ₃ , %	26.63
Fe ₂ O ₃ , %	8.27
CaO, %	5.84
MgO, %	2.79
TiO ₂ , %	1.05
SO ₃ , %	0.93
P ₂ O ₅ , %	0.87
K ₂ O + Na ₂ O, %	1.16

The obtained data show that the main macroelements of coal ash are acidic and amphoteric oxides of silicon, aluminum and iron, the total concentration of which is 85 %, which is comparable with similar data obtained in [7] (90 %).

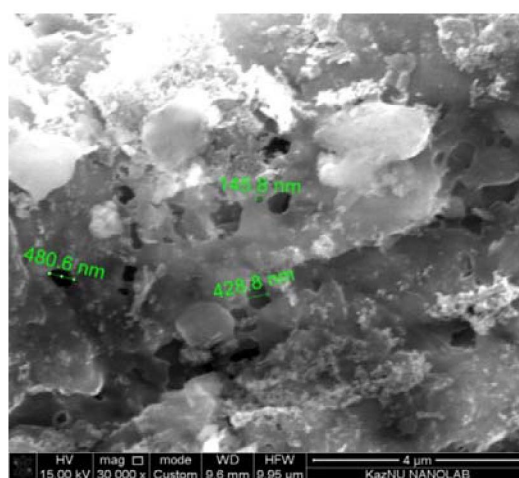
To characterize the ash activity of the studied coal and their stability during decomposition, the basicity modulus (M_0) was calculated using the known formula [25] as the ratio of the sum of the contents of basic alkaline earth metal oxides to the sum of silicon and aluminum oxides (in %): $M_0 = (CaO + MgO)/(SiO_2 + Al_2O_3)$.

The calculation results showed that the modulus of basicity is 0.112 which makes it possible to assign these samples to the class of acid ashes ($M_0 < 1$), which causes their absence properties [4].

Electron microscopic images of coal ash samples, presented in figure 3, demonstrate the morphological features of the samples, whence it is seen that the ash surface is heterogeneous and represents an amorphous and dense structure and is characterized in some places by flaky inclusions. Most ash particles have an irregular shape (flat, acute-angled). The surface relief of the particles has a high degree of roughness and pores of various geometric shapes with sizes up to about 500 nm (figure 3, b), which corresponds to macropores with sizes > 50 nm (according to the classification of pores adopted by the International Union of Theoretical and Applied Chemistry (IUPAC)).



a) $\times 10\,000$



б) $\times 30\,000$

Figure 3 – Electron microscopic images of the ashes of Maikuben coal: a) initial ash; b) ash after EM treatment

The results of the analysis of micrographs show that after the EM treatment, the ash acquires a more developed surface and porous structure.

The obtained data on X-ray phase analysis (table 3) show that the presence of two crystalline phases of the main ash-forming elements, α -quartz and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), is common to all the ash samples studied. This coincides with the literature data obtained in the study of the phase composition of coal ash from other deposits, where these minerals are also the main crystalline phases [4-6]. As a result of the ED treatment of the ashes, kaolinite and anhydrite are removed and mineral phases with the content of rare metals Ge, Li, Ga are additionally formed (table 3). This effect of the electric discharge is apparently due to the fact that when the pulsed high-voltage voltage is applied to the ashes, a simultaneous influence and a complex mechanism of all the effective factors of the electrohydraulic effect occur, which lead to the breaking of sorption and peripheral chemical bonds and the formation of new compounds.

Table 3 – Mineral composition of Maikuben coal

Phase name	Chemical composition		
	initial ash	ash after EM treatment	ash after ED treatment
α -Quartz	SiO_2	SiO_2	SiO_2
Mullite	$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$
Kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	–
Hematite	Fe_2O_3	Fe_2O_3	–
Anhydrite	$\text{Ca}(\text{SO}_4)$	$\text{Ca}(\text{SO}_4)$	–
Aluminum Germanium Oxide Hydroxide	–	–	$\text{Al}_2\text{GeO}_4(\text{OH})_2$
Octalithium hexakis(gallosilicate)dibromide	–	–	$\text{Li}_8(\text{GaSiO}_4)_6\text{Br}_2$

Bulk density, pH of the aqueous extract, adsorption activities on iodine and methyl orange for samples of coal ash (in its original form, after the EM and ED treatments) were determined in accordance with [26,27]. The results of the analysis are shown in table 4.

Table 4 – Physical and chemical characteristics of the ashes of the Maikuben coal

Name of the indicator	Ash in its original form	Ash after EM treatment	Ash after ED treatment
Bulk density, g/cm^3	0.75	0.810	0.90
Methyl orange adsorption activity, %	65.00	70.10	69.50
pH of the aqueous extract	9.20	8.86	4.27

Highest values of bulk density and methyl orange adsorption activity has ash after EM and ED treatments, confirming the data obtained by microscopic analysis of samples (figure 3), where electro-magnetic treatment leads to a more developed surface and porous structure.

Table 5 presents the results of measurements of specific surface area and specific pore volume (by limiting filling) of the studied coal ash samples.

Table 5 – Adsorption characteristics of coal ash

Name	Specific surface area, m^2/g	Specific pore volume, cm^3/g
Ash in its original form	23.876	0.036
Ash after EM treatment	37.914	0.055
Ash after ED treatment	38.639	0.057

The data obtained show that the coal ash is a porous material. EM treatment of ash samples contributes to a noticeable increase in the specific surface area (≈ 1.6 times) and the specific volume of pores (≈ 1.5 times). At the same time, the ED treatment of ash (after EM treatment) almost does not lead to a noticeable change in the values of the specific volume of pores and specific surface. The results of the analysis of adsorption characteristics of initial ash samples are approximately consistent with similar parameters obtained in [3,7].

The results of the analysis of the volumetric distribution of particle sizes for different values of bulk density $D_v(10)$, $D_v(50)$, $D_v(90)$ (10%, 50%, 90% of particles from the total amount respectively) are presented in table 6.

Table 6 – The results of the analysis of the particle size of Maikuben coal ash

Name of the indicator	Uniformity	Dv(10), μm	Dv(50), μm	Dv(90), μm
Ash in its original form	1.484	7.91	129	612
Ash after EM treatment	4.771	1.41	7.08	75.3
Ash after ED treatment	1.903	7.07	101	603

As can be seen from the results of the analysis, when exposed to coal ash by electric discharge, there is a slight decrease in particle size (1.1-1.3 times) ash for for all volumetric distributions. At the same time, the EM treatment of coal ash leads to a more significant decrease in the particle size of the ash as compared to the electric discharge treatment, especially for the average distribution of $D_v(50)$, where the particle size decreases by 18.2 times (129-7.08 μm). The consequence of the effective influence of the EM treatment of coal ash on particle size reduction is an increase in the specific surface and specific pore volume. This fact is confirmed by the obtained data on the adsorption characteristics of the ash (table 5).

Conclusion. Thus, the study of the effects of electrophysical effects on Maikuben coal ash showed that EM treatment effectively mainly affects the particle size and adsorption properties of coal ash, while ED treatment mainly affects the mineralogical composition of coal ash. The use of electrophysical treatment of coal ash is of particular scientific and practical interest, since it allows for the qualitative preparation of this material for its further thermochemical processing in order to leach valuable components such as rare metals, silica, alumina.

Acknowledgement. The present work was carried out within the framework of the scientific and technical program No. IRN BR05236359 on the topic: "Scientific and technological support of coal processing and production of high-conversion products of carbon chemistry", funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan.

Б. Т. Ермагамбет, Н. У. Нургалиев, Н. А. Маслов, Л. Д. Абылгазина, А. А. Сыздыкова

«Көмір химиясы және технология институты» ЖШС, Нұр-Сұлтан, Қазақстан

МАЙКУБЕН КЕН ОРНЫНЫҢ КӨМІР КҮЛІНІҢ ФИЗИКАЛЫҚ-ХИМИЯЛЫҚ ҚАСИЕТТЕРІНЕ ЭЛЕКТРОФИЗИКАЛЫҚ ӘСЕРДІҢ САЛДАРЫ

Аннотация. Жұмыста Шоптыкөл кен орнындағы (Майкүбен бассейні, Қазақстан) көмір күлін электрофизикалық өңдеу барысында оның физика-химиялық қасиеттеріне тигізетін әсері зерттелген. Көмір күлі алдын ала электромагниттік аппаратта (күл бөлшектерін ұсақтау үшін) өңделді, одан соң магнит түйіршіктерімен араластырып (диаметрі 2-3 мм) жұмыс камерасына жіберілді (индуктор ішіне орнатылды), ал ұнтақтау процесі 8 минуттан 3 рет жүргізілді. Содан кейін сумен араласқан (1/2 массалық қатынаста) күлді кернеуі 30 кВ-қа дейін жоғары вольтты электр разрядты қондырғыда күл бөлшектеріндегі химиялық байланыстардың әлсіреуі және/ немесе бұзу мақсатында 3 минут өңдейді. Электрофизикалық өңдеуге дейін және өңдеуден кейін көмір күлінің физика-химиялық сипаттамаларын көп элементті аспаптық нейтронды-активтендіруді талдау әдісімен көп каналды амплитудалық импульсті («Канбегга»компаниясы) анализаторда (микроэлементтік құрамын элементтік талдау үшін), SEM электронды микроскопындағы энергодисперстік рентген-спектроскопиялық әдіспен SEM (Quanta 3D 200i) сканерлеуші растрлы электронды микроскопта (күлдің құрылымы мен күл бөлшектерінің өлшемін зерттеу және макроэлементтік құрамына талдау жасау үшін), RigakuMiniFlex 600 дифрактометрмен рентгендік дифракция әдісімен (минералды құрамды талдау үшін), лазерлі дифракция әдісімен MalvernMastersizer 3000 құрылғысында (күл бөлшектерінің өлшемі бойынша көлемдік таралуын талдау үшін), SorbtometerM анализаторында («Катакон»компаниясы) Брунауэр-Эмметт-Теллер (БЕТ) (нақты беттік ауданды және кеуектердің нақты көлемін анықтау үшін) зерттелді. Зерттелген көмірдің микроэлементін талдау нәтижелері кальций, барий, стронций, натрий сияқты металдардың көп мөлшерде (0,08-ден 3,54%-ға дейін), ал қалған элементтер өте аз мөлшерде (0,01% немесе одан аз) бар екендігін көрсетті, әсіресе күміс, тантал, алтын, бром, лютеций өте аз мөлшерде болады. Көмір күлінің макроэлементтік құрамын талдау нәтижелері көрсеткендей, негізгі макроэлементтер кремнийдің, алюминий мен темірдің қышқылдық және амфотерлі оксидтері болып табылады, олардың жалпы концентрациясы 85 %-ды құрайды. Зерттеліп отырған күл үшін есептелген негіздік модуль (M_0) 0,112 болды, бұл оны қышқыл күлге ($M_0 < 1$) жатқызуға мүмкіндік береді, бұл тұтқыр қасиеттердің болмауына себепкер болады. Күлдің электронды микроскопиялық талдауы бөлшектердің беттік рельефінің кедір-бұдырлығының жоғары екендігін және өлшемі 500 нм-ге дейін, бұл өлшемдері > 50 нм макрокеуектерге сәйкес келетін әртүрлі геометриялық формалардың бар екендігін көрсетті. Сонымен қатар, электромагниттік өңдеуден кейін күл

дамыған беткі және кеуекті құрылымға ие болады. Рентгендік дифракцияның нәтижелері күлдің негізгі элементтерінің екі кристалды фазасының, α -кварц пен муллиттің ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) болуы барлық зерттелген күл сынамаларына ортақ екенін көрсетті. Электрлік разрядты өңдеу нәтижесінде күлден каолинит және ангидрит жойылып, құрамында сирек кездесетін металдар Ga, Ge, Li бар минералды фазалары қосымша құрылатындығы анықталды. Бұл сорбциялық және перифериялық химиялық байланыстардың бұзылып, жаңа байланыстардың пайда болуына алып келетін электрогидравликалық эффекттің барлық әсер етуші факторларының бір уақытта әсер етуі мен күрделі механизмнің әсерінен пайда болады. Көмір күлінің метилоранж үлгілері бойынша сусымалы тығыздықты және адсорбциялық белсенділікті талдау нәтижелері электромагниттік және электр разрядты өңдеуден кейінгі параметрлердің мәні бастапқы күлмен салыстырғанда едәуір үлкен екенін көрсетті, бұл электромагниттік өңдеу неғұрлым дамыған бетке және кеуекті құрылымға алып келетіндігін көрсететін электронды микроскопия арқылы алынған мәліметтермен сәйкес келеді. Көмір күлінің зерттелген үлгілерінің меншікті бетінің ауданын және кеуектің меншікті көлемін (максималды толтыру бойынша) зерттеу нәтижелері көмір күлінің кеуекті материал екенін көрсетті. Күлдің сынамаларын электромагниттік өңдеу меншікті беттік ауданының (1,6 есе) және кеуектердің меншікті көлемінің (1,5 есе) артуына ықпал ететіндігін көрсетті. Сонымен бірге күлді одан әрі электрлі разрядты өңдеу (электромагниттік өңдеуден кейін) іс жүзінде кеуек көлемі мен меншікті бетінің мәндерінің айтарлықтай өзгеруіне әкелмейді. Бөлшектердің көлемдік тығыздықтың $D_v(10)$, $D_v(50)$, $D_v(90)$ әртүрлі мәндеріндегі (бөлшектердің жалпы мөлшерінен тиісінше 10%, 50%, 90%) өлшемдері бойынша көлемдік таралуының анализі көрсеткендей электр разрядымен өңдеуден кейін барлық көлемді таралулар үшін күлдің бөлшектерінің өлшемі жай азаятындығын көрсетті (1,1-1,3 есе). Сонымен қатар, көмір күлін электромагниттік өңдеу электр разрядты өңдеумен салыстырғанда тазартумен салыстырғанда күлдің бөлшектерінің өлшемінің едәуір азаюына әкеледі, әсіресе $D_v(50)$ орташа таралуы кезінде тиімді, онда бөлшектердің мөлшері 18,2 есе азаяды (129-дан 7 мкм-ге дейін). Осылайша, электрофизикалық әсер етудің көмір күліне әсерін зерттеу электромагниттік өңдеу күл бөлшектері мен адсорбциялық қасиеттеріне ұнтақтаудың әсері бар екендігін көрсетті. Сонымен қатар электр разрядының әсері негізінен шикізаттың минералогиялық құрамына әсер етеді. Көмір күлін электрофизикалық өңдеуді қолдану ғылыми және практикалық қызығушылық тудырады, өйткені бұл құнды өнімдерді (кремний, глинозем, сирек кездесетін металдар және т.б.) толықтай алу үшін және/немесе технологиялық режимдерді «жұмсарту» мақсатында күлді одан әрі өңдеуге сапалы дайындауға мүмкіндік береді.

Түйін сөздер: көмір, күл, электромагниттік өңдеу, электрразрядты өңдеу, химиялық құрамы, физикалық-химиялық сипаттамалары.

Б. Т. Ермагамбет, Н. У. Нурғалиев, Н. А. Маслов, Л. Д. Абылғазина, А. А. Сыздықова

ТОО «Институт химии угля и технологии», Нур-Султан, Казахстан

ВЛИЯНИЕ ЭЛЕКТРОФИЗИЧЕСКОГО ВОЗДЕЙСТВИЯ НА ФИЗИКО-ХИМИЧЕСКИЕ ХАРАКТЕРИСТИКИ ЗОЛЫ УГЛЯ МАЙКУБЕНСКОГО МЕСТОРОЖДЕНИЯ

Аннотация. В работе исследовано влияние электрофизической обработки золы угля месторождения «Шоптыколь» (Майкубенский бассейн, Казахстан) на ее физико-химические характеристики. Предварительно угольную золу обрабатывали на электромагнитном аппарате (для тонкого измельчения частиц золы), в котором золу предварительно перемешивали с магнитными гранулами (диаметром 2-3 мм) и выгружали в рабочую камеру (установленную внутри индуктора), и процесс измельчения проводили 3 раза по 8 минут. Затем золу, смешанную с водой (в массовом соотношении 1/2 соответственно), подвергали воздействию на высоковольтной электроразрядной установке с напряжением до 30 кВ в течение 3 минут для ослабления и/или разрыва химических связей в частицах золы. Физико-химические характеристики золы угля до и после электрофизической обработки исследовали методами многоэлементного инструментального нейтронно-активационного анализа на многоканальном амплитудном анализаторе импульсов (компания «Капбегга») (для элементного анализа на содержание микроэлементов), энергодисперсионной рентгеновской спектроскопии на сканирующем растровом электронном микроскопе SEM (Quanta 3D 200i) с приставкой для энергодисперсионного анализа (для изучения структуры и размерности золы и анализа на содержание макроэлементов), рентгеновской дифракции на дифрактометре Rigaku MiniFlex 600 (для анализа на минеральный состав), лазерной дифракции на приборе Malvern Mastersizer 3000 (для анализа объемного распределения частиц золы по размерам), Брунауэра-Эммета-Теллера (БЭТ) на анализаторе Sorbtometer M (компания «Катакон») (для определения удельной поверхности и удельного объема пор). Результаты микроэлементного анализа исследуемого угля показали наличие в наибольшем количестве (от 0,08 до 3,54 %) таких металлов, как кальций, барий, стронций, натрий, а остальные элементы присутствуют в очень малых количествах (от 0,01 % и менее), особенно серебро, тантал, золото, бром, лутеций. Результаты анализа на содержание макроэлементов в

золе угля показали, что основными макроэлементами являются кислые и амфотерные оксиды кремния, алюминия и железа, общая концентрация которых составляет 85 %. Рассчитанный модуль основности (M_0) для исследуемой золы составил 0,112, что позволяет ее отнести к классу кислых зол ($M_0 < 1$), что обуславливает отсутствие вяжущих свойств. Электронно-микроскопический анализ золы показал, что рельеф поверхности частиц имеет высокую степень шероховатости и поры различной геометрической формы размером примерно до 500 нм, что соответствует макропорам с размерами >50 нм. Кроме того, после электромагнитной обработки зола приобретает более развитую поверхностную и пористую структуру. Результаты рентгеновской дифракции показали, что общим для всех исследуемых образцов золы является наличие двух кристаллических фаз основных золообразующих элементов – α -кварц и муллит ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). Установлено, что в результате электроразрядной обработки золы удаляются каолинит и ангидрит и дополнительно образуются минеральные фазы с содержанием редких металлов Ga, Ge, Li, что, по-видимому, обусловлено одновременным влиянием и сложным механизмом всех действующих факторов электрогидравлического эффекта, приводящих к разрыву сорбционных и периферических химических связей и к образованию новых соединений. Результаты анализа насыпной плотности и адсорбционной активности по метилоранжу образцов золы угля показали, что значения данных параметров после электромагнитной и электроразрядной обработок заметно больше по сравнению с исходной золой, что совпадает с данными, полученными методом электронной микроскопии, где электромагнитная обработка приводит к более развитой поверхностной и пористой структуре. Результаты измерений удельной площади поверхности и удельного объема пор (по предельному заполнению) исследуемых образцов золы угля показали, что зола угля представляет собой пористый материал. Электромагнитная обработка образцов золы способствует заметному увеличению удельной поверхности (в 1,6 раз) и удельного объема пор (в 1,5 раза). Вместе с тем, дальнейшая электроразрядная обработка золы (после электромагнитной обработки) почти не приводит к заметному изменению значений удельного объема пор и удельной поверхности. Анализ объемного распределения частиц по размерам при различных значениях объемной плотности $D_V(10)$, $D_V(50)$, $D_V(90)$ (соответственно 10%, 50%, 90% частиц от их общего количества) показал, что после обработки электрическим разрядом происходит незначительное уменьшение размеров частиц (в 1,1-1,3 раза) золы для всех объемных распределений. Вместе с тем, электромагнитная обработка золы угля приводит к более существенному уменьшению размеров частиц золы по сравнению с электроразрядной обработкой, особенно для среднего распределения $D_V(50)$, где размер частиц уменьшается в 18,2 раза (от 129 до 7 мкм). Таким образом, исследование влияния электрофизического воздействия на золу угля показало, что на измельчение частиц золы и адсорбционные свойства эффективнее оказывает электромагнитная обработка. Вместе с тем, электроразрядное воздействие преимущественно оказывает воздействие на минералогический состав сырья. Использование электрофизической обработки золы угля представляет определенный научный и практический интерес, так как позволяет осуществить качественную подготовку золы для ее дальнейшей переработки с целью более полного извлечения ценных продуктов (кремнезема, глинозема, редкоземельных металлов и др.) и/или «смягчения» технологических режимов проведения данного процесса.

Ключевые слова: уголь, зола, электромагнитная обработка, электроразрядная обработка, химический состав, физико-химические характеристики.

Information about authors:

Yermagambet B.T., Director of LLP "Institute of Coal Chemistry and Technology", Doctor of Chemical Science, Professor; bake.yer@mail.ru; <https://orcid.org/0000-0003-1556-9526>

Nurgaliyev N.U., Leading Researcher of LLP "Institute of Coal Chemistry and Technology", Candidate of Chemical Science; nurgaliyev_nao@mail.ru; <https://orcid.org/0000-0001-9171-2238>

Maslov N.A., Chief Specialist for Energy and Automation of LLP "Institute of Coal Chemistry and Technology"; nike.6484@mail.ru; <https://orcid.org/0000-0003-2550-6123>

Abylgazina L.D., Junior Researcher of LLP "Institute of Coal Chemistry and Technology", Master of Engineering Sciences; lelya_1501@mail.ru; <https://orcid.org/0000-0002-0949-9616>

Syzdykova A.A., Junior Researcher of LLP "Institute of Coal Chemistry and Technology"; botasyzydykova2212@gmail.com; <https://orcid.org/0000-0003-4649-9479>

REFERENCES

[1] Adeeva L.N., Borbat V.F. (2009) Zola TJeC – perspektivnoe syr'e dlja promyshlennosti, *Vestnik Omskogo universitetata*, 2: 141-151 (in Russ.).

[2] Dhadse S., Kumari P., Bhagia L.J. (2008) Fly ash characterization, utilization and government initiatives in India – a review, *Journal of Scientific and Industrial Research*, 67(1): 11-18, <http://nopr.niscair.res.in/handle/123456789/729> (in Eng).

- [3] Mihajlov Ju.L. (2001) Fiziko-himicheskie issledovaniya processov vyshchelachivaniya mikrokomponentov zoly ot szhiganiya uglej Jekibastuzskogo bassejna: avtoref. kand. him. nauk, Omsk. 2001. P. 20.
- [4] Gerk S.A., Smoliy V.A. (2013) Study of the composition and structure of waste fuel and energy complex using electron microscopic and elemental analysis [Issledovanie sostava i struktury othodov toplivno-jenergeticheskogo kompleksa s primeneniem jelektronno-mikroskopicheskogo i jelementnogo analiza], News of universities, North Caucasus region, Technical Sciences Series, 4: 76-79 (in Russ.).
- [5] Khairul Nizar Ismail, Kamarudin Hussin, Mohd Sobri Idris (2007) Physical, Chemical & Mineralogical Properties of Fly Ash, *Journal of Nuclear and Related Technology*, 4: 47-51 (in Eng.).
- [6] Khairul Nizar Ismail, Mustafa Al Bakri A.M., Rafiza A.R., Kamarudin H., Alida A., Zarina Y. (2014) Study on Physical and Chemical Properties of Fly Ash from Different Area in Malaysia, *Key Engineering Materials*, 594-595: 985-989 (in Eng.).
- [7] Tauanov Z., Abylgazina L., Spitas C., Itskos G., Inglezakis V. (2017) Mineralogical, Microstructural and Thermal Characterization of Coal Fly Ash Produced from Kazakhstani Power Plants. International Conference on Materials Sciences and Nanomaterials. IOP Conf. Series: Materials Science and Engineering, 230: 43-49 (in Eng.).
- [8] Poltoranina A.P., Cherkashina K.Y., Kluikova Y.I. (2013) Investigation of the physical and chemical properties of the ash of Kuzbass coal with the purpose of its utilization [Issledovanie fiziko-himicheskikh svoystv zoly uglej Kuzbassa s cel'ju ee utilizacii], Proceedings of the XVII Intern. Symposium them. Acad. M.A. Usov students and young scientists: "Problems of geology and exploration of mineral resources", Tomsk: Publishing House of Tomsk Polytechnic University. P. 181 (in Russ.).
- [9] Wang J, Li D, Ju F, Han L, Chang L, Bao W. (2014) Supercritical hydrothermal synthesis of zeolites from coal fly ash for mercury removal from coal derived gas, *J Fuel Process. Technol.*, 136: 96-105 (in Eng.).
- [10] Duta A., Visa M. J. (2015) Simultaneous removal of two industrial dyes by adsorption and photocatalysis on a fly-ash-TiO₂ composite, *J Photochem Photobiol*, 306: 21-30 (in Eng.).
- [11] Visa M., Chelaru AM. (2014) Hydrothermally modified fly ash for heavy metals and dyes removal in advanced wastewater treatment, *Applied Surface Science*, 303: 14-22. DOI:10.1016/j.apsusc.2014.02.025 (in Eng.).
- [12] Jha B., Singh D.N. (2014) A three step process for purification of fly ash zeolites by hydrothermal treatment, *Applied Clay Science*, 90: 122-29. DOI:10.1016/j.clay.2013.12.035 (in Eng.).
- [13] Xie J., Wang Z., Wu D., Kong H. (2014) Synthesis and properties of zeolite/hydrated iron oxide composite from coal fly ash as efficient adsorbent to simultaneously retain cationic and anionic pollutants from water, *Fuel*, 116: 71-76. DOI:10.1016/j.fuel.2013.07.126 (in Eng.).
- [14] Menshov P.V., Khlupin Y.V., Nalesnik O.I., Makarovskikh A.V. (2014) Ash and Slag Waste as a Secondary Raw Material, *Procedia Chemistry*, 10: 184-191. DOI: 10.1016/j.proche.2014.10.032 (in Eng.).
- [15] Shabarov A.N., Nikolayeva N.V. (2016) Complex utilization of treatment wastes from thermal power plants [Kompleksnoe ispol'zovanie othodov pererabotki teplojelektrostantsij], Journal of Mining Institute, 220: 607-610. DOI: 10.18454/PMI.2016.4.607 (in Eng.).
- [16] Borbat V. F., Mikhailov Y.L., Adeyeva L.N., Golovanova O. A. (2000), *Chemistry and chemical technology*, 1: 102 (in Russ.).
- [17] Liu K., Xue J.L., Zhu J. (2012) In: *Light Metals, Suarez CE, John Wiley & Sons Inc.*, 6: 201 (in Eng.).
- [18] Bai G.H., Qiao Y.H., Shen B., Chen S.L. (2011) *Fuel Process. Technol.*, 92: 1213 (in Eng.).
- [19] Xiang-Yang C., Xin-zhe L., Qui-li Z., Hong-zhou M.A., Hin Z. (2010) Influence of NaCl on dechromization of Cu-Cr-Al alloy in H₃PO₄ solution, *Trans Nonferr Met Soc China*, 20 (1): 123-127. DOI: 10.1016/S1003-6326(09)60108-4 (in Eng.).
- [20] Arroyo F., Font O., Chimenos J.M., Pereira C.F., Querol X., Coca P. (2014) IGCC fly ash valorisation. Optimisation of Ge and Ga recovery for an industrial application, *Fuel Processing Technology*, 124: 222-227. DOI: 10.1016/j.fuproc.2014.03.004 (in Eng.).
- [21] Hernandez-Exposito A., Chimenos J.M., Fernandez A.I., Font O., Querol X., Coca P., Garcia P.F. (2006) Ion flotation of germanium from fly ash aqueous leachates, *Chemical Engineering journal*, 118: 69-75. DOI: 10.1016/j.cej.2006.01.012 (in Eng.).
- [22] Torralvo F.A., Fernández-pereira C. (2011) Recovery of germanium from real fly ash leachates by ion-exchange extraction, *Minerals Engineering*, 24: 35-41. DOI: 10.1016/j.mineng.2010.09.004 (in Eng.).
- [23] Yermakov A.N. (1988) Analytical chemistry of rare elements [Analiticheskaja himija redkih jelementov], Collection of scientific papers, Moscow: Science. P. 245 (in Russ.).
- [24] Yermagambet B.T., Nurgaliyev N.U., Abylgazina L.D., Maslov N.A., Kasanova Zh.M., Kasenov B.K. (2018) Methods for extraction of valuable components from ash-and-slag coal wastes, News of the National Academy of Sciences of the Republic of Kazakhstan, Series Chemistry and Technology, 6(432): 67-78. <https://doi.org/10.32014/2018.2518-1491.28> (in Eng.).
- [25] Guzhelev E.P., Usmanskiy Y.T. (1998) Rational use of ash CHP: The results of scientific research [Racional'noe primeneniye zoly TJEC: Rezul'taty nauchno-prakticheskikh issledovaniy]. Omsk State University. P. 238 (in Russ.).
- [26] Smirnov A.D. (1982) Sorption water purification [Sorbcionnaya ochistka vody], Leningrad: Chemistry. P. 168 (in Russ.).
- [27] Kabulov A.T., Nechipurenko S.V., Efremov S.A. (2015) Works of the Kol Scientific Center of the Russian Academy of Sciences, 5(31): 527 (in Russ.).